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Furnishing amine-functionalized MOFs with the β -amidoketone group by post-synthetic modification

William J. Gee,* Laura K. Cadman, Harina Amer Hamzah, Mary F. Mahon,* Paul R. Raithby and Andrew D. Burrows*

Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY (UK).

KEYWORDS post-synthetic modification, coordination polymer, metal-organic framework, PSM, MOF.

Supporting Information Placeholder

ABSTRACT: The post-synthetic modification (PSM) of amino-functionalized MOFs to those bearing pendant β -amidoketone arms using diketene is herein reported. Three unique MOF families demonstrate the scope of this transformation, which is both atom-economical and yields high conversions. In each case crystallinity was retained, and instances of exceptional solid-state ordering were observed in the PSM products, which has allowed detailed crystallographic characterization in multiple instances.

Metal-organic frameworks (MOFs) are hybrid inorganic-organic materials that show exceptional promise across a range of applications,¹ such as catalysis,² gas adsorption, separation and storage,³ vessels for crystallographically viewing chemical reactions,⁴ and both magnetic⁵ and optical devices.⁶ Many of the physical properties behind these applications rely on predetermined functional groups that are present within the pores of MOF architectures. While MOF pores can be furnished with simple functional groups by prefunctionalizing the organic linker, the scope of such chemistry has been limited by the harsh synthetic protocols inherent to many MOF syntheses.⁷ This limitation can be overcome by adopting a post-synthetic modification (PSM) strategy, in which the chemical and physical properties of MOF materials are modified in a heterogeneous fashion.^{7,8} This strategy has been essential for placement of reactive functional groups within MOF pores that could not otherwise be synthetically achieved using a prefunctionalization approach.

One of the main means of facilitating PSM reactions is covalent modification, wherein the organic linkers are reacted after MOF formation. Notable examples include oxidation of sulfur-tagged MOFs with dimethyldioxirane,⁹ amine induced ring-opening reactions of sultones or aziridines,¹⁰ conversion of amines to reactive thio- and isocyanates,¹¹ and 'click' chemistry performed on azides derived from amine groups.¹² In each instance more complex functionalities were produced after identification of a suitable organic reaction or reagent, ultimately providing new materials and properties.⁷ Herein we report the discovery of a new PSM reaction involving the reaction of diketene with MOFs prefunctionalized with amine groups (Figure 1). The reaction yields β -amidoketones in a facile, high-yielding and atom-economical fashion. This reaction is of further significance owing to the non-carcinogenic nature of diketene,¹³ the known metal-chelating ability of the resulting β -amidoketone group,¹⁴ and the prevalence of solid-state ordering observed in many of the resulting PSM products, allowing direct crystallographic characteriza-

tion for multiple modified MOFs. Aminated MOFs have previously been reacted with maleic anhydride and glyoxal, but in those cases the resultant functionalities were less ordered.¹⁵

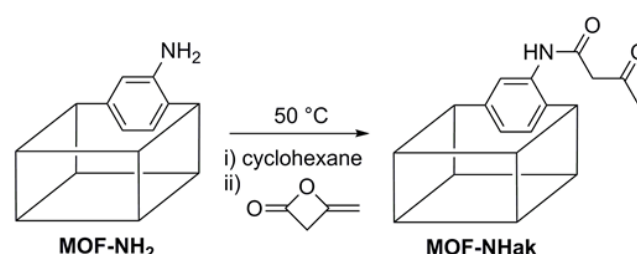


Figure 1. PSM reaction of post-activated amino-functionalized MOFs (MOF-NH₂) with diketene to yield β -amidoketones (MOF-NHak).

To best demonstrate the applicability of this new β -amidoketone forming PSM reaction, three well-known MOFs and a mixed-ligand system (Section S1, ESI) were targeted: DMOF-1-NH₂¹⁶ [Zn₂(bdc-NH₂)₂(dabco)],¹⁷ [Zn₂(bdc)(bdc-NH₂)(dabco)], (bdc = 1,4-benzenedicarboxylate); IRMOF-3¹⁸ [Zn₄O(bdc-NH₂)₃]; and Fujita's crystalline sponge (FCS),⁴ FCS-NH₂ [Zn₃I₆(tpt)₂]·atp-NH₂, (tpt = 2,4,6-tris(4-pyridyl)-1,3,5-triazine, atp-NH₂ = aminotriphenylene). The PSM conversions ranged from 82% to quantitative as judged by ¹H-NMR spectroscopy.

DMOF-1-NHak (1): ¹H-NMR spectroscopy was used to gauge the percentage conversion of bdc-NH₂ to the PSM ligand, 3-[(1,3-dioxobutyl)amino]-benzenedicarboxylate (bdc-NHak) on digested samples of [Zn₂(bdc-NH₂)_{0.32}(bdc-NHak)_{1.68}(dabco)]·DMF (DMOF-1-NHak, **1**). When assigning the conversion percentage, aromatic signals were generally used to aid comparison with the parent ligands. ¹H-NMR analysis of a bulk crystalline sample of **1** yielded both keto/enol tautomerism of the terminal ketone group, and the overall PSM conversion percentage. This data is presented in Table 1 with that of **2** and **3**. Full ¹H-NMR assignment for the conversion of each MOF species may be found as ESI (S2-S3).

Table 1 Summary of ¹H-NMR results for 1-3

MOF	Digestion media	NHak (k:e) ratio ^a	Conv. (%)
1	(30 : 1) DMSO- <i>d</i> ₆ : DCI (35% wt in D ₂ O)	10 : 1	84
2	(30 : 1) DMSO- <i>d</i> ₆ : DCI (35% wt in D ₂ O)	10 : 1	82
3	DMF- <i>d</i> ₇	3.3 : 1	100

^aketo/enol ratio of digested bdc-NHak assigned from integrals of the *ortho*-ring singlet resonance from each tautomer.

The PSM reaction resulted in no outward changes to the crystalline appearance of **1**. The framework crystallizes in the monoclinic space group $C2/m$, with the asymmetric unit containing half of a zinc atom, half of a bdc ligand (comprised of a 16:84 bdc-NH₂:bdc-NHak ratio), quarter of a dabco ligand and some guest solvent. The structure contains the zinc paddlewheel secondary building unit capped by dabco ligands (Fig. 2), forming the pillared MOF motif that is typical of this type of material.^{16,17}

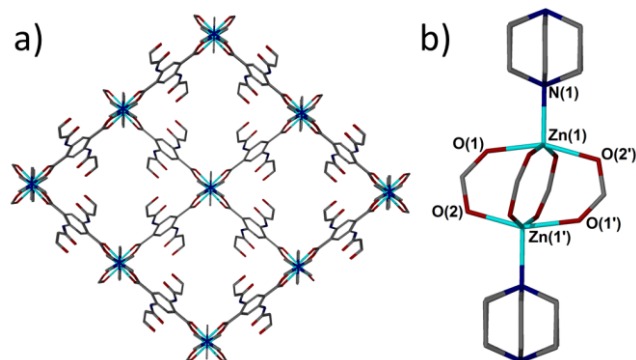


Figure 2. a) View down the crystallographic c axis showing the PSM groups disordered over two sites within the channels of DMOF-1-NHak. b) The paddlewheel coordination environment of Zn²⁺ in DMOF-1-NHak.

Crystallographic analysis of DMOF-1-NHak (**1**) revealed that the ordering of the PSM product within the pores was sufficient to visualize all but the methyl terminus of the –NHak tag. The terminal methyl group on this PSM arm could not be reliably located owing to smearing of the electron density with increasing distance from the ligand core. This was further evidenced by increasing atomic displacement parameter (ADP) size proceeding along the –NHak chain. This observation is exceptional for functionalized MOFs given that electron density pertaining to functional groups present within MOF pores typically proves far too diffuse to allow crystallographic modelling. In this model the ligand moiety straddles a crystallographic inversion center, which necessarily means that the –NH₂ and –NHak tags are disordered between two positions on the phenyl ring. Beyond the anchoring nitrogen atom the PSM chain possesses atom occupancies of 42% reflecting the 84% conversion of the amino groups in the PSM reaction. The dabco carbons similarly exhibits disorder, which is unsurprising considering this entity does not have mirror symmetry along the N...N vector. Full discussion of the disorder observed for **1**, as well as that of a 1:1 bdc/bdc-NH₂ mixed-ligand variant can be found as ESI (Sections S4-S5).

A recent study of mixed ligand bdc/bdc-NH₂ variants of DMOF-1 identified a distorted square pore geometry in which the ligands were offset when viewed down the crystallographic c axis, yet here it is the [Zn₂(CO₂)₄] secondary building unit that distorts (Fig. 2b) which allows the ligands to align in an eclipsed fashion.¹⁷ The zinc ions within the paddlewheel motif are misaligned by *ca* 15° relative to N...N vector of the dabco ligands, which likely provides a more amenable pore cavity to enclose the larger functional group within the channels. Ultimately, this distorts the regular square grid topology of the framework as described by the aforementioned study.¹⁷

IRMOF-3-NHak (2): Spectroscopic analyses provided evidence for the PSM reaction of IRMOF-3 with diketene. Qualitative evidence of the reaction to **2** could be observed microscopically, as single crystals of IRMOF-3 became opaque and yellow in color post-reaction. Despite excellent diffraction of the crystals when irradiated with X-rays, a lack of ordering of the PSM group within the MOF pores prevented reliable modelling of more than

the initial nitrogen atom. Consequently, the obtained crystal data offers no insight beyond the previously reported IRMOF-3, and has not been included here. Two prominent new bands were observed in the infrared spectrum at 1755 and 1662 cm⁻¹, which correspond to the newly formed keto and amido groups. As with the DMOF species **1**, loss of the primary amine bands at 3474 and 3351 cm⁻¹ from the parent MOF were also evident post-reaction.

The ¹H-NMR spectrum of bdc-NHak obtained from **2** was similar to with that of the digested DMOF-1 species **1** (Fig. S1). In each instance, the aromatic signals are shifted downfield relative to the reference acid, H₂bdc-NH₂, upon undergoing the PSM reaction. This effect is most pronounced for the hydrogen in the *ortho* position relative to the amine group, which shifts from δ 7.62 ppm to *ca* δ 9 ppm. The remaining aromatic hydrogens are also deshielded in each instance, albeit to a lesser degree. Evidence for the carboxylic acid and amido hydrogens were typically absent from the ¹H-NMR spectrum, owing to facile exchange with deuterium chloride of the digestion media, however evidence for the methylene and terminal methyl groups could typically be observed in the region from δ 2 - 3 ppm.

FCS-NHak (3): While the triphenylene group complicated the aromatic region of the ¹H-NMR spectrum, a considerable quantity of information could still be garnered. The use of DMF-d₇ allowed visualization of both the keto and enol amido N-H resonances at δ 10.7 and 10.5 ppm respectively, giving direct evidence for PSM group formation. The enolic OH group was also observed at δ 14.1 ppm. By contrast, the methylene and terminal methyl group of the keto PSM arm were observed at δ 3.95 and 2.50 ppm, respectively. No evidence of unreacted primary amine cartridge was evident, and of the species found within the pores, one equivalent of unreacted diketene was assigned based on the characteristic terminal methylene resonances at δ 5.01 and 4.74 ppm, and a multiplet that integrated for two hydrogens at δ 4.39 ppm that was attributed to the methylene group of the oxetane ring.

This system provided a second visual means of outwardly observing the PSM reaction. Electronic changes in the aminotriphenylene ‘cartridge’ upon PSM reaction within FCS-NH₂ resulted in a color change in the crystals from red to yellow (Fig. S9). This is consistent with other reports of chemical reactions undertaken in Fujita’s crystalline flasks.⁴ After screening upwards of 20 samples, suitable single crystals of FCS-NHak were found and analyzed. The asymmetric unit was found to contain three zinc centers, six iodides, two tridentate neutral triazine-based ligands, a post-synthetically modified triphenylene molecule and some diffuse guest solvent (Fig. 3).

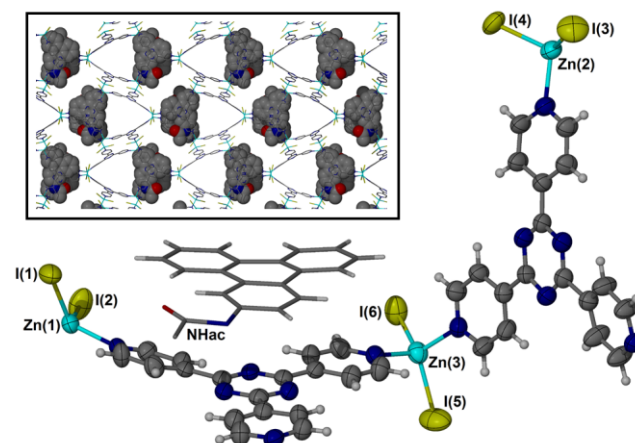


Figure 3. The modelled asymmetric unit of FCS-NHak. The PSM chain could only be reliably modelled to the methylene group (shown here as NHAc). Ellipsoids are shown with 50% probability. Diffuse solvent molecules are omitted for clarity.

Resolving MOF framework **3**, which comprises repeating three Zn₂ nodes linked by two tpt linkers, from the X-ray diffraction data was relatively straightforward. The derivatized triphenylene guest is sandwiched between two tpt ligands, each from distinct, interpenetrated layers of the framework (Fig. 3, inset). Two types of large pore are present, of which only one contains the PSM tag of atp-NHAc, this being consistent with previous reports.⁴ Disorder of the triphenylene group over two proximate positions was observed (full details in ESI). Consequently, it was not possible to reliably locate the terminal CH₃CO portion of the sidechain and thus it was omitted from the refinement along with the hydrogen atoms attached to methylene bridge carbon (*i.e.* the carbon terminus of NHAc shown in Fig. 3). The site occupancy of these atoms was treated as unity, based on ¹H-NMR evidence for 100% PSM conversion.

This post-synthetic reaction is exceptional in that single crystallinity of the products was universally retained using these protocols, and the resultant modified group was directly crystallographically observable in three of the four cases studied. These features are extremely valuable, as powder X-ray diffraction patterns of MOF frameworks are typically unchanged upon PSM, and hence only serve to gauge the crystallinity of the products. A crystallographic window of the PSM region broadens the application of these materials to paramagnetic species that would interfere with ¹H-NMR analyses, and time-resolved crystallographic processes.

In summary we have identified and evaluated the scope of a new PSM reaction that has exciting implications for MOF chemistry. The transformation imparts consistently high conversions (>80%), is atom-economical, synthetically easily achieved, and applicable to a range of common MOF families. **The resultant β-amidoketone group is a known metal chelating group with acidic character, opening the MOF pore to a host of further transformations. We are currently investigating these reactions on a range of β-amidoketone-functionalized MOFs.** This combination of synthetic ease and useful functionality will recommend this PSM transformation for widespread implementation within the MOF community.

ASSOCIATED CONTENT

Supporting Information

Full experimental details, details of mixed ligand MOF, Zn₂(bdc)(bdc-NH₂)(dabco)], ¹H-NMR assignment of all MOF digests, crystallographic refinement details and discussion. CCDC 1426996-1426998, contain the supplementary crystallographic data for this paper. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

A. D. Burrows E-mail: A.D.Burrows@bath.ac.uk

Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

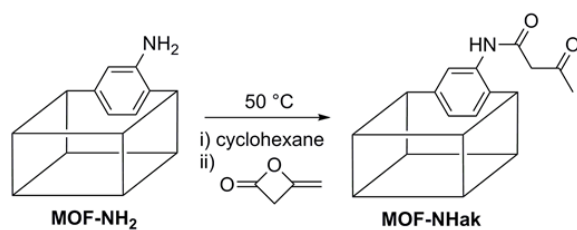
The authors declare no competing financial interests.

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The post-synthetic modification (PSM) of amino-functionalized MOFs to pendant β-amidoketone arms using diketene has been demonstrated with three unique MOF families. The PSM reaction is both atom-economical and yields high conversion percentages. In each case crystallinity was retained, and instances of exceptional solid-state ordering were observed in the PSM products.
